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(54) Title  
BAYER LIQUOR TREATMENT

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(57) Claim

1. In the Bayer process as hereinbefore defined for forming alumina, an improvement comprising contacting a process stream containing organic material as hereinbefore defined with less than 100 g/l manganese dioxide ( $MnO_2$ ) or an equivalent amount of a partially reduced form of manganese dioxide such as ( $Mn_2O_3$ ) to oxidize organic material.

AUSTRALIA  
Patents Act 1990

COMPLETE SPECIFICATION  
STANDARD PATENT

Applicant(s):

THE BROKEN HILL PROPRIETARY COMPANY LIMITED

Invention Title:

BAYER LIQUOR TREATMENT

The following statement is a full description of this invention, including the best method of performing it known to me/us:

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# BAYER LIQUOR TREATMENT

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The present invention relates to the Bayer process for producing alumina from bauxite.

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The term "Bayer process" as used throughout the specification is understood to mean a process which comprises the following basic steps: (a) digesting bauxite in sodium hydroxide to form a solution containing sodium aluminate, (b) precipitating aluminium hydroxide from the solution, and (c) calcining the precipitate to form alumina, and which may include further optional steps in addition to steps (a), (b) and (c). The solution, or any other liquor present in steps (a), (b) or (c) or in any of

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the optional steps, is commonly referred to as "Bayer liquor".

The adverse effects of organic material, and in particular sodium oxalate, contained in bauxite ores on the Bayer process is well documented in the patent and non-patent literature.

The term "organic material" as used throughout the specification is understood to mean compounds containing carbon other than carbonates.

The known adverse effects of organic material on the Bayer process include:

1. foaming of Bayer liquor under agitation, causing poor utilization of tank capacity and generation of caustic aerosols into the atmosphere which pose a safety hazard;
2. stabilization of supersaturated Bayer liquor with the result that comparatively lower productivity is obtained from the same initial concentration of aluminate ion in solution;
3. an increase in viscosity of the Bayer liquor, resulting in poorer settling of red muds and poorer filtration of aluminium hydroxide;
4. a lowering of the causticity of the Bayer liquor, thereby increasing consumption of sodium hydroxide;
5. undesirable soda contamination of the product

alumina; and

6. precipitation of excessive amounts of fine aluminium hydroxide which adversely affects the particle size distribution of the alumina.

There have been a number of proposals for ameliorating the problems caused by organic material.

One proposal developed by the applicant is based on the use of manganese dioxide to oxidize organic material to carbonates. The experimental and pilot plant work carried out by the applicant in relation to the proposal concentrated on the reduction in total organic material and found that elevated temperatures (greater than 200°C) and relatively high loadings of manganese dioxide (greater than 200 g/l) are required to have a quantifiable impact on the reduction of the concentration of organic material in Bayer liquor.

An object of the present invention is to provide an improved method of alleviating the adverse affects caused by organic material in Bayer liquor.

According to the present invention there is provided, in the Bayer process as hereinbefore described for forming alumina, an improvement comprising contacting a process stream containing organic material as hereinbefore described with less than 100 g/l manganese dioxide ( $\text{MnO}_2$ ) or an equivalent amount of a partially reduced form of manganese dioxide such as ( $\text{Mn}_2\text{O}_3$ ) to oxidize organic material.

The present invention is based on the realization that

selective oxidation of organic material in a Bayer liquor, without necessarily reducing the level of organic material, with relatively low concentrations of manganese dioxide ore, compared to the levels previously thought to be necessary to have an impact on the levels of organic material in the Bayer liquor, resulted in substantial increases in alumina yield and product quality (measured by soda content in the alumina).

10        It is preferred that the concentration of manganese dioxide be less than 80 g/l.

It is particularly preferred that the concentration of manganese dioxide be less than 60 g/l.

15        Typically, the concentration of manganese dioxide is less than 40 g/l.

20        It is preferred that the manganese dioxide comprises manganese dioxide ore.

It is preferred that the process stream be at a predetermined temperature of 175°C or more.

25        It is particularly preferred that the predetermined temperature be 200°C or more. Typically, it is preferred that the predetermined temperature be 240°C or more.

30        In situations where the process stream to be treated is less than the predetermined temperature, it is preferred that the process comprises heating the process stream to the predetermined temperature.

It is preferred that the process stream comprises spent

Bayer liquor from the aluminium hydroxide precipitation step in the Bayer process.

5 It is particularly preferred that the process stream comprises evaporated spent Bayer liquor from the aluminium hydroxide precipitation step and the subsequent evaporation step in the Bayer process.

10 It is particularly preferred that the improvement further comprises removing sodium oxalate from spent Bayer liquor after contacting the organic material with manganese dioxide.

15 The experimental work on which the present invention is based concentrated on the effect on alumina yield and product quality of relatively low manganese dioxide levels, which were sufficient to selectively oxidize organic material. In this regard, it is noted that in some respects the experimental work was a significant departure  
20 from the previous experimental work of the applicant which was based on the assumption that a net reduction in the level of organic material would be necessary to produce an improvement in alumina yield and product quality and therefore concentrated on maximizing the removal of all  
25 organic material by conversion to carbonates.

The following is a summary of the experimental work on which the present invention is based.

30 Batch treatment procedure for liquors

The work was carried out using both green liquors and evaporated spent liquors from alumina plants. The liquors contained between 25 and 30 g/l total organic carbon

(hereinafter referred to as "TOC") and approximately 40 g/l sodium carbonate. The green liquors contained 190-200 g/l sodium hydroxide and the spent liquors contained 200-255 g/l sodium hydroxide (reported as equivalent  $\text{Na}_2\text{CO}_3$ ).

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The liquors treated with  $\text{MnO}_2$  ore (premium grade fines from the Groote Eylandt Mine) were stirred and heated with the required amount of  $\text{MnO}_2$  ore in a Parr 1 US Gallon Autoclave. Typically, 2 litres of liquor were stirred with  
10 50 g/l of  $\text{MnO}_2$  ore and heated to the required temperature, which was held for 30 minutes. After the required heating time, cold water was pumped through a cooling coil within the autoclave to prevent any further reactions.

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After treatment, all the liquors were adjusted ("balanced") to have the same final concentrations of alumina, caustic and carbonate in solution. No changes were made to the organic material composition of the liquors after  $\text{MnO}_2$  treatment, except when sodium oxalate  
20 was precipitated from treated spent liquors prior to bauxite digestion.

#### Aluminium hydroxide precipitation tests

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An evaluation of the  $\text{MnO}_2$  treatment process was carried out using a standard two day aluminium hydroxide precipitation test which included staged temperature drops between 80°C and 60°C.

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In this regard, after balancing, bauxite digestion and clarification, each liquor sample was divided into 200 ml fractions and the fractions were placed into 250 ml polyethene bottles and heated in a tumbling water bath before being seeded with seed hydrate and tumbled. Sample



bottles were removed periodically and the solids were separated from the liquors. Both the liquors and the solids were analysed to determine the amount of alumina precipitated and the quality of the resultant product.

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The results of the analyses on liquor samples that are presented in Table 1 hereinafter and in Figures 3, 5, and 6 are expressed as an "alumina/caustic ratio", (A/C). The A/C ratio is a ratio of the dissolved alumina and the sodium hydroxide in the liquors at any given time. It can readily be appreciated that the A/C ratio is a measure of the yield obtained during precipitation. Specifically, the lower the final A/C ratio the higher the yield.

#### 15 Analyses performed

The liquors were analysed using procedures commonly employed by the alumina industry. The alumina, caustic and carbonate concentrations were determined by automatic titration using a modified Watts and Utley titration method disclosed in a paper entitled "Sodium Gluconate as a Complexing Agent in the Volumetric Analysis of Aluminium Compounds" published in Analytical Chemistry 28 (1956) 1731 to 1735. The oxalate, sodium chloride and sodium sulfate concentrations were determined by ion chromatography and total organic carbon using a Barnstead or Dohrmann total organic carbon analyser. The solid aluminium hydroxide precipitate was analysed for soda and trace elements by X-ray Fluorescence Spectrometry; the alumina was analysed for manganese by ICP spectrometry, and particle sizing was carried out using a Malvern MasterSizer.

### Treatment of green liquors

5        A series of experiments was carried out on green  
liquors to investigate the consumption of sodium hydroxide  
with  $\text{MnO}_2$  ore loadings and the temperature dependence of  
the sodium hydroxide consumption. In this regard, the  
oxidation of organic material by manganese dioxide consumes  
10       sodium hydroxide as a result of the formation of  
appropriate compounds and thus the change in sodium  
hydroxide is a measure of the level of oxidation.  
The result of the experiments are shown in Figures 1 and 2.

15       It is evident from Figure 1 that at relatively low  $\text{MnO}_2$   
ore loadings, i.e. less than 100 g/l, there is a reasonable  
level of sodium hydroxide consumption thus indicating that  
the levels of manganese dioxide ore were sufficient to  
oxidise certain of the organic material present.

20       A series of experiments was carried out in which green  
liquors were treated with 50 g/l  $\text{MnO}_2$  ore at  
different temperatures over the range 145-250°C. The  
liquors were then subjected to aluminium hydroxide  
25       precipitation tests after being "balanced" as previously  
mentioned. The results are shown in Table I below and in  
Figure 3.

Table I precipitation after MnO<sub>2</sub> treatment

5	Test	Treatment Conditions	Final A/C ratio	Na <sub>2</sub> O content
	1	Untreated	0.440	0.48
	2	175°C no MnO <sub>2</sub>	0.442	0.49
	3	145°C + MnO <sub>2</sub>	0.436	0.45
10	4	175°C + MnO <sub>2</sub>	0.429	0.43
	5	200°C + MnO <sub>2</sub>	0.424	0.43
	6	225°C + MnO <sub>2</sub>	0.423	0.39
	7	250°C + MnO <sub>2</sub>	0.421	0.39

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Table I shows the A/C ratio and the soda concentration at the end of the precipitation tests.

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Figure 3 shows the precipitation rate curves for Tests 1, 4, and 7 in Table 1.

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The results show a marked increase in precipitation performance with increased treatment temperature. The MnO<sub>2</sub> treatment process clearly gives higher alumina yields (up to 7% relative increase) and leads to a substantial reduction in soda concentration of the alumina, which is an important factor in product quality.

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Further work was carried out at 175°C as this provided a significant yield improvement and was close to the operating temperature for many alumina refineries. The series of experiments conducted at 175°C are represented as a response surface in Figure 4. The plot illustrates clearly that, with low MnO<sub>2</sub> ore loading and reaction times

in excess of 10 minutes, it is mainly  $\text{MnO}_2$  ore loading and not reaction time that determines the extent of the treatment and thus the maximum yield possible. At  $175^\circ\text{C}$ , it was found that doubling the reaction time (30 to 60 minutes) led to a 0.5% relative increase in yield and an increase in ore loading to 50 to 100 g/l resulted in a relative yield increase of 5%.

#### Treatment during digestion

The results of the work on green liquors demonstrated that it was possible to increase alumina yield and improve product quality using  $\text{MnO}_2$  ore treatment of the Bayer liquor. However, it is thought that the treatment of the clarified green liquor is probably not feasible in an operating alumina plant because of the additional heating and cooling steps of the green liquor that would be required prior to precipitation. Therefore, ideally the  $\text{MnO}_2$  treatment of a green liquor should take place during the digestion stage with the ore being added together with the bauxite and the reacted ore separated with the red mud from the process stream.

A sample of "liquor to digestion" was put through both a "normal" bauxite digestion and a combined bauxite digestion/manganese dioxide treatment at  $175^\circ\text{C}$ . The results are presented in Figure 5 and show an increase in yield for the treated liquor although not as significant as that observed for the green liquor treatment.

The presence of normally non-extractable organic material in the bauxite is probably the cause of the reduced effectiveness of the  $\text{MnO}_2$  treatment. It is likely that the oxidising power of the  $\text{MnO}_2$  had been partially

consumed by the non-extractable organic material and by the easily oxidisable groups which would otherwise be oxidised during the normal process of bauxite digestion.

5     Treatment of evaporated spent liquors

A series of aluminium hydroxide precipitation tests was carried out on samples of evaporated spent liquors heated to 250°C and:

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(a) treated with 50 g/l  $\text{MnO}_2$  ore;

(b) untreated; and

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(c) partly treated with 50 g/l  $\text{MnO}_2$  ore and partly untreated.

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It is noted that sodium oxalate was removed from each liquor sample after mixing and balancing prior to bauxite digestion. Sodium oxalate removal involved "seeding" the liquor with 25 g/l of AR grade sodium oxalate, stirring for 1 hour at room temperature, and filtration. It is also noted that the liquors were used to digest bauxite and not aluminium hydroxide prior to precipitation, and thus the

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liquors were contacted with a fresh source of organic materials, potentially containing active organic materials, prior to precipitation.

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The results of the experiments are shown in Figure 6. The results confirm the result of the previous work that an increase in yield can be achieved with  $\text{MnO}_2$  treatment of Bayer liquor. In addition, the results for a mixed 50% treated/50% untreated liquor, when compared with the results for the untreated and 100% treated liquors, show

that the increase in yield reflected in the Figure is almost directly proportional to the fraction of the liquor which had been treated with  $\text{MnO}_2$ . The direct proportionality indicates that only a proportion of the "active" organic materials removed during  $\text{MnO}_2$  treatment was returned to the liquor during each digestion with bauxite.

The work of Bird et al in a paper entitled "The Effect of Four Common Bayer Liquor Impurities on Alumina Solubility" published in Light Metals 1983 pp 65-82 showed that the effective yield of an alumina precipitation circuit could be modelled by the following equations:

$$\text{Yield} = (\text{Initial A/C} - \text{Final A/C}) \times C \text{ g/l}$$

$$\begin{aligned} \text{Final A/C} = & [0.4987 - 0.049799 \ln (\text{cycle hrs})] + \\ & [(\text{Na}_2\text{CO}_3/\text{C}) \times 0.14] + [(\text{NaCl}/\text{C}) \times 0.17] + \\ & [(\text{Na}_2\text{SO}_4/\text{C}) \times 0.1] + [(\text{Organic "S"}/\text{C}) \times 0.195] \end{aligned}$$

where

C = NaOH concentrations

cycle hrs = total precipitation time

For the evaporated spent liquor used in this study, the second equation set out above simplifies to:

$$\text{Final A/C} = 0.4277 = [(1.98 \times 10^{-3}) \times \text{TOC}]$$

where TOC is the total organic carbon content of the liquor.

The yield predicted by the Bird equation is shown in

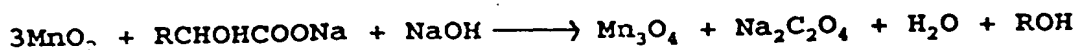
Figure 7 for TOC values between 0 and 30 g/l. Figure 7 also shows the actual yields for an untreated evaporated spent liquor, and  $\text{MnO}_2$  treated evaporated spent liquor, a 50% treated liquor and a synthetic "balanced" liquor with no TOC content. The yield prediction for the non- $\text{MnO}_2$ -treated liquors is very good whilst the  $\text{MnO}_2$  treated liquor gives a yield close to that of the synthetic, zero TOC liquor.

It can be concluded therefore that the  $\text{MnO}_2$  treatment, although removing only relatively small amounts of TOC (1-2 g/l), removed or altered most of the organic species responsible for the reduction in yield. The results shown in Figure 7 are typical of those obtained in testing liquors from low temperature alumina refineries.

#### Discussion and conclusions

The results of the experimental work show that the  $\text{MnO}_2$  treatment process comprising contacting Bayer liquor with relatively low levels of manganese dioxide ore is capable of removing or altering organic material responsible for the stabilisation of alumina in Bayer liquor and thus contributes to higher yields of alumina for each liquor cycle. The results also show that the  $\text{MnO}_2$  treatment process is capable of improving alumina quality (measured by reduced  $\text{Na}_2\text{O}$  concentration).

However, it is noted that the selective oxidation of organic material as a result of treatment of Bayer liquor with  $\text{MnO}_2$  does result in the formation of sodium oxalate. By way of example, the equation set out below shows the oxidation of a carboxylic acid to result in the formation of sodium oxalate.



where R is an aliphatic or aromatic hydrocarbon group.

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In view of the known adverse effect of sodium oxalate on the Bayer process it is preferable that the  $\text{MnO}_2$  treatment process includes the removal of sodium oxalate.

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With the above in mind, a preferred embodiment of the present invention shown in Figure 8 comprises:

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(a)  $\text{MnO}_2$  treatment carried out on spent liquor (preferably an evaporated spent liquor which has an increased concentration of "active" organic materials) from the precipitation step of the Bayer process; and

(b) a sodium oxalate removal step.

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With reference to Figure 8, the  $\text{MnO}_2$  treatment plant comprises pairs of stirred reactor vessels (the size and number of which are dependent on the side-stream flow) designed to operate on a batch basis, a number of heat exchangers, an oxalate crystalliser and filter and a

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boiler.

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In use, the batch reactor vessels are charged with spent liquor which has added to it an appropriate charge of  $\text{MnO}_2$  ore and is heated to the desired process temperature ( $250^\circ\text{C}$ ) and held at that temperature for 30 minutes. At the conclusion of the foregoing treatment cycle the spent liquor is circulated through a heat exchanger to pre-heat a charge to the second reactor. The treated spent liquor is cooled further with process water and then is discharged to



the crystalliser where sodium oxalate is precipitated and subsequently filtered. The filtered treated spent liquor is then returned to the digestion circuit.

- 5        An alternative arrangement (not shown) comprises a reactor vessel designed to operate on a continuous basis.

10       Many modifications may be made to the preferred embodiments described above without departing from the spirit and scope of the present invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. In the Bayer process as hereinbefore defined for forming alumina, an improvement comprising contacting a process stream containing organic material as hereinbefore defined with less than 100 g/l manganese dioxide ( $\text{MnO}_2$ ) or an equivalent amount of a partially reduced form of manganese dioxide such as ( $\text{Mn}_2\text{O}_3$ ) to oxidize organic material.

2. The improvement defined in claim 1, wherein the concentration of manganese dioxide is less than 80 g/l.

3. The improvement defined in claim 2, wherein the concentration of manganese dioxide is less than 60 g/l.

4. The improvement defined in claim 3, wherein the concentration of manganese dioxide is less than 40 g/l.

5. The improvement defined in any one of the preceding claims, wherein the manganese dioxide comprises manganese dioxide ore.

6. The improvement defined in any one of the preceding claims, wherein the process stream is at a predetermined temperature of 175°C or more.

7. The improvement defined in claim 6, wherein the predetermined temperature is 200°C or more.

8. The improvement of claim 7, wherein the predetermined temperature is 240°C or more.

9. The improvement defined in any one of the preceding

claims, wherein the process stream comprises spent Bayer liquor from the aluminium hydroxide precipitation step in the Bayer process.

5        10. The improvement defined in any one of claims 1 to 8, wherein the process stream comprises evaporated spent Bayer liquor from the aluminium hydroxide precipitation step and the subsequent evaporation step in the Bayer process.

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11. The improvement defined in any one of the preceding claims, further comprising removing sodium oxalate from spent Bayer liquor after contacting the organic material with manganese dioxide.

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Dated this 13th day of October 1992

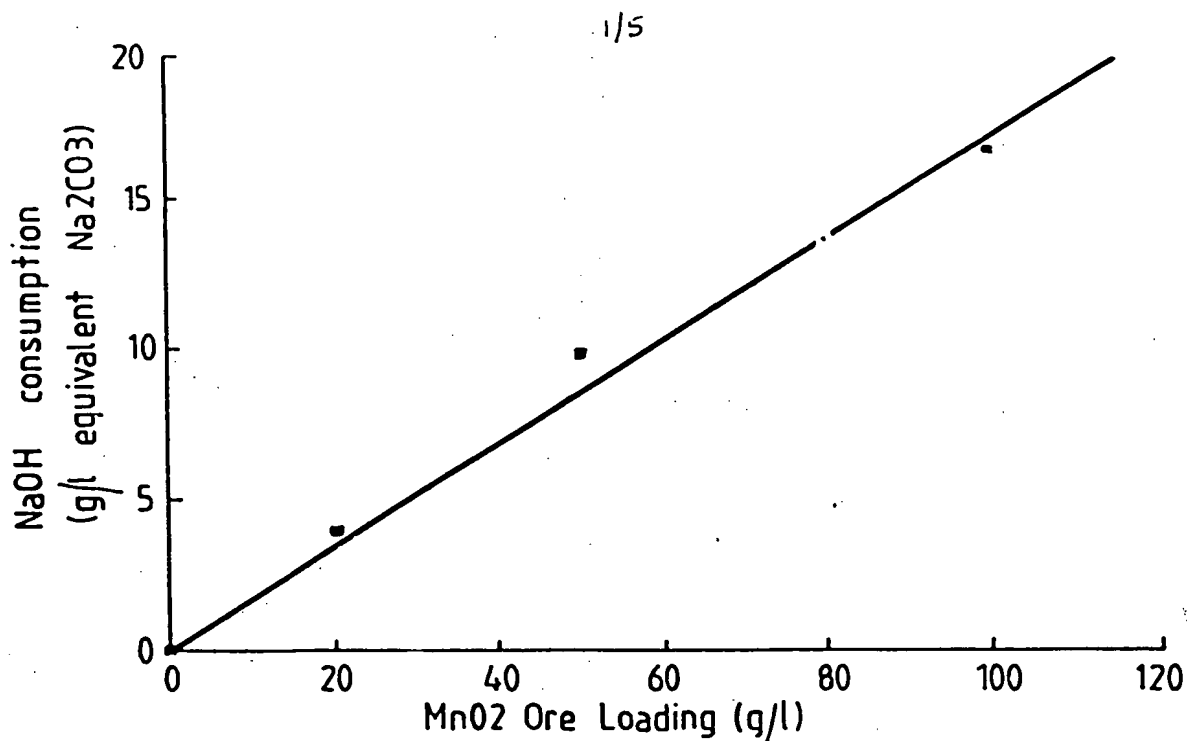
THE BROKEN HILL PROPRIETARY COMPANY LIMITED

By Its Patent Attorneys

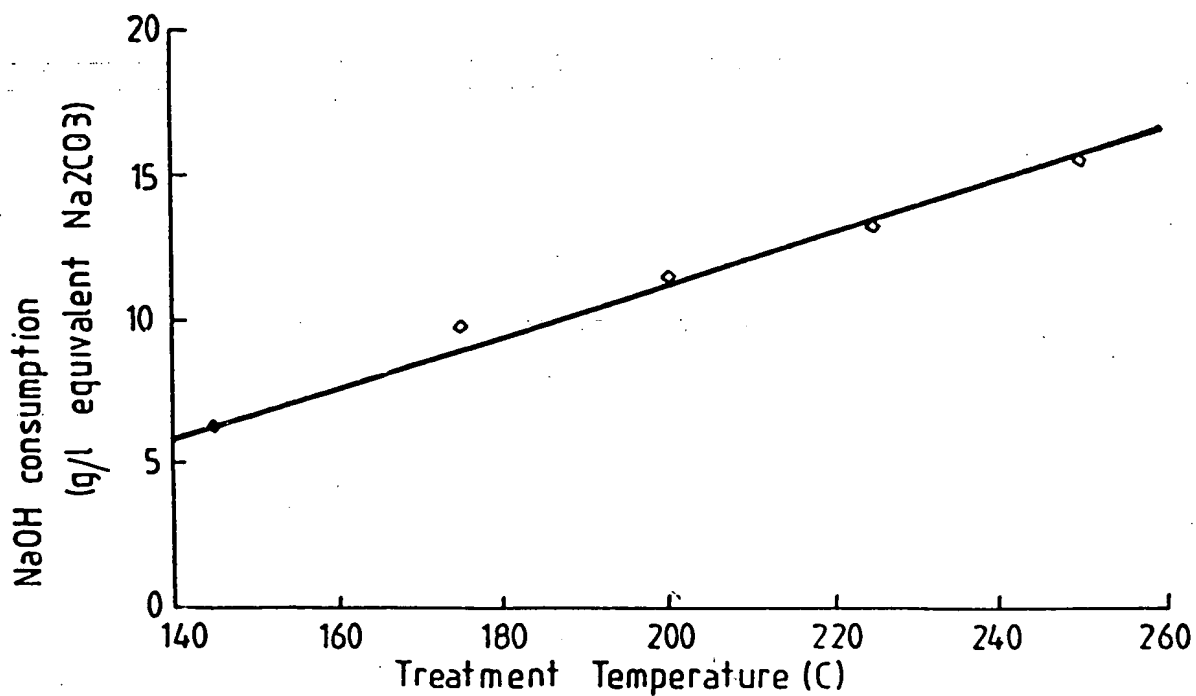
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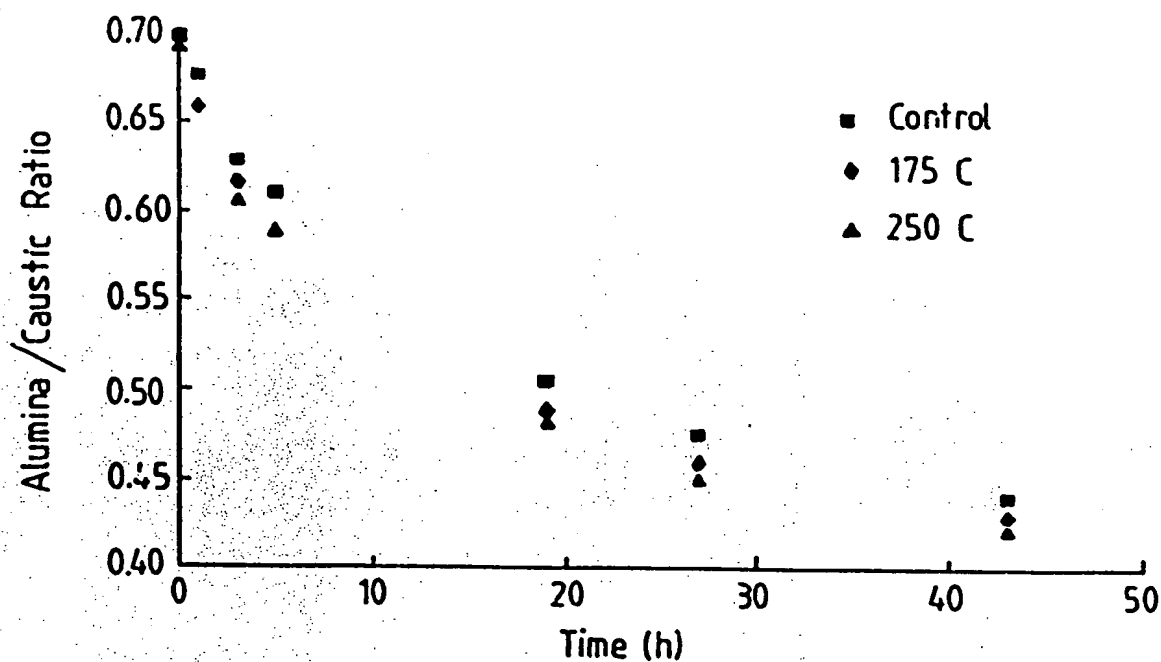
Fellows Institute of Patent Attorneys of Australia.



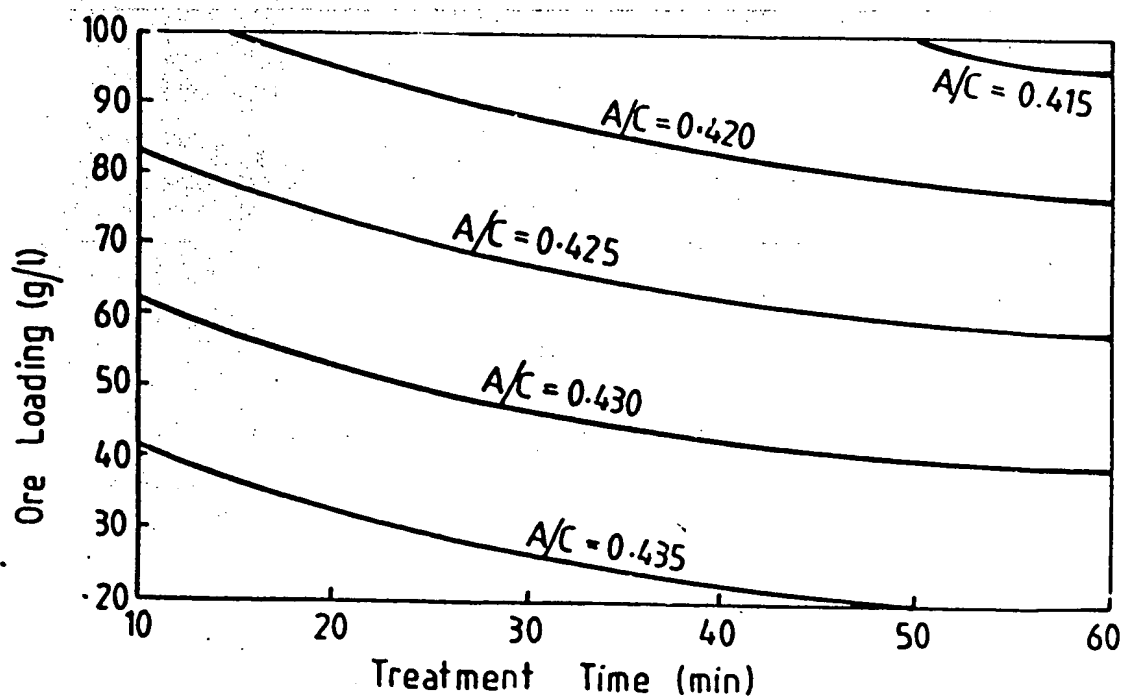
III. 1. Consumption of caustic soda during  $\text{MnO}_2$  Treatment - influence of ore loading



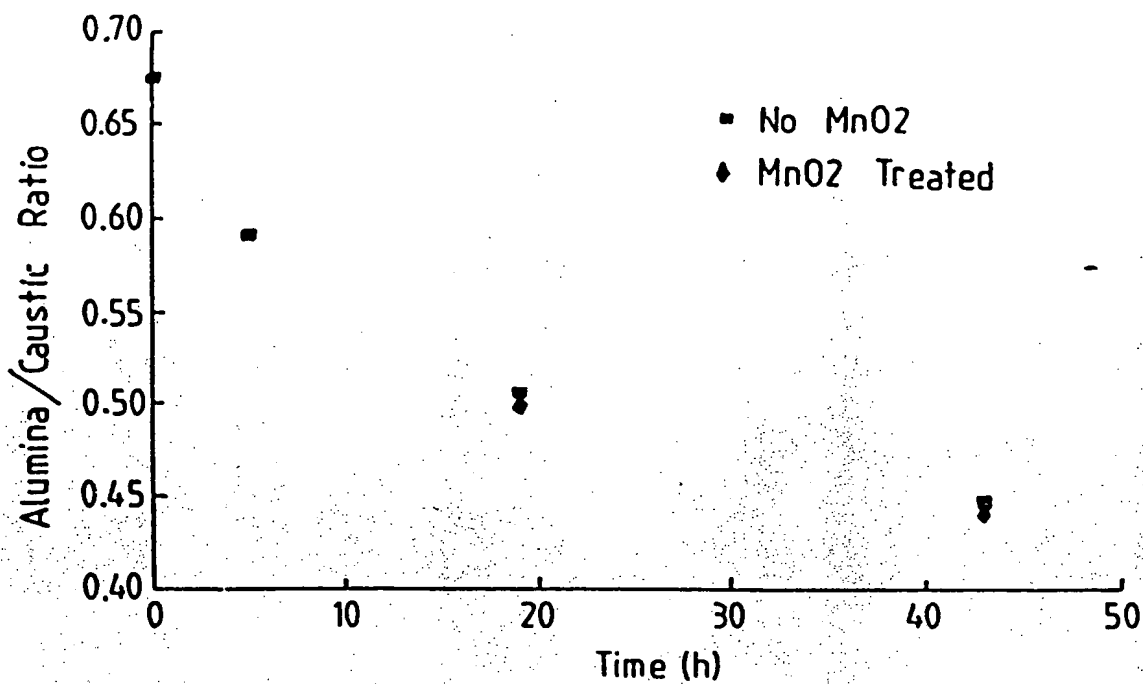
III. 2. Consumption of caustic soda during  $\text{MnO}_2$  Treatment - Influence of treatment temperature



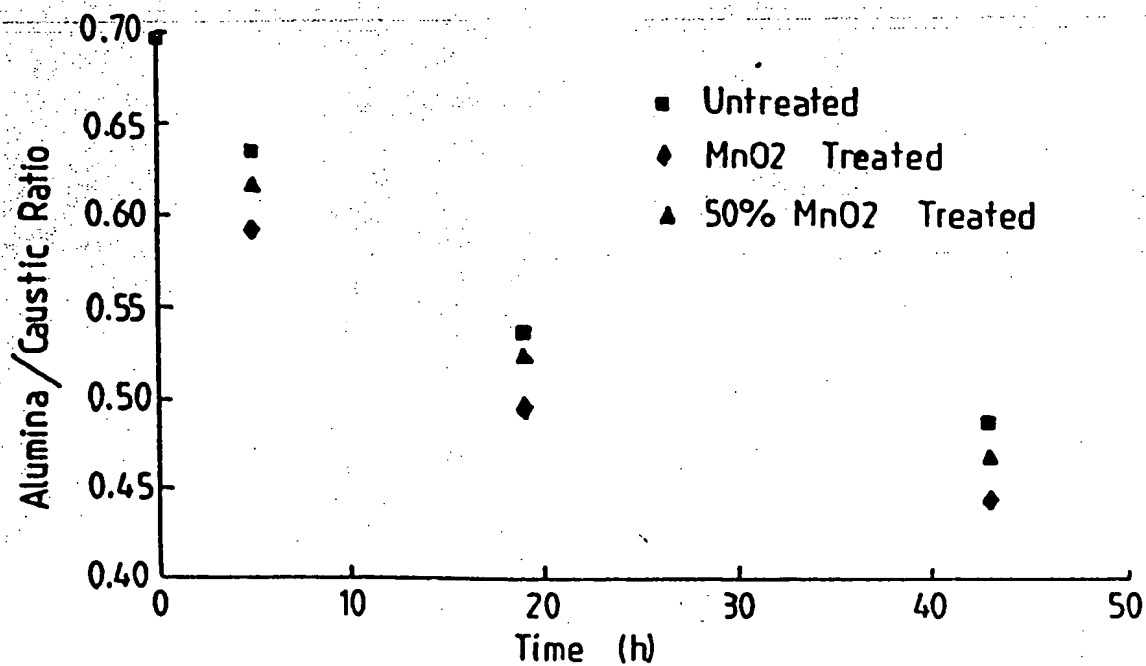
III. 3. Precipitation rate curves



III. 4. Response surface for final A/C ratio as a function of ore loading and reaction time at 175°C



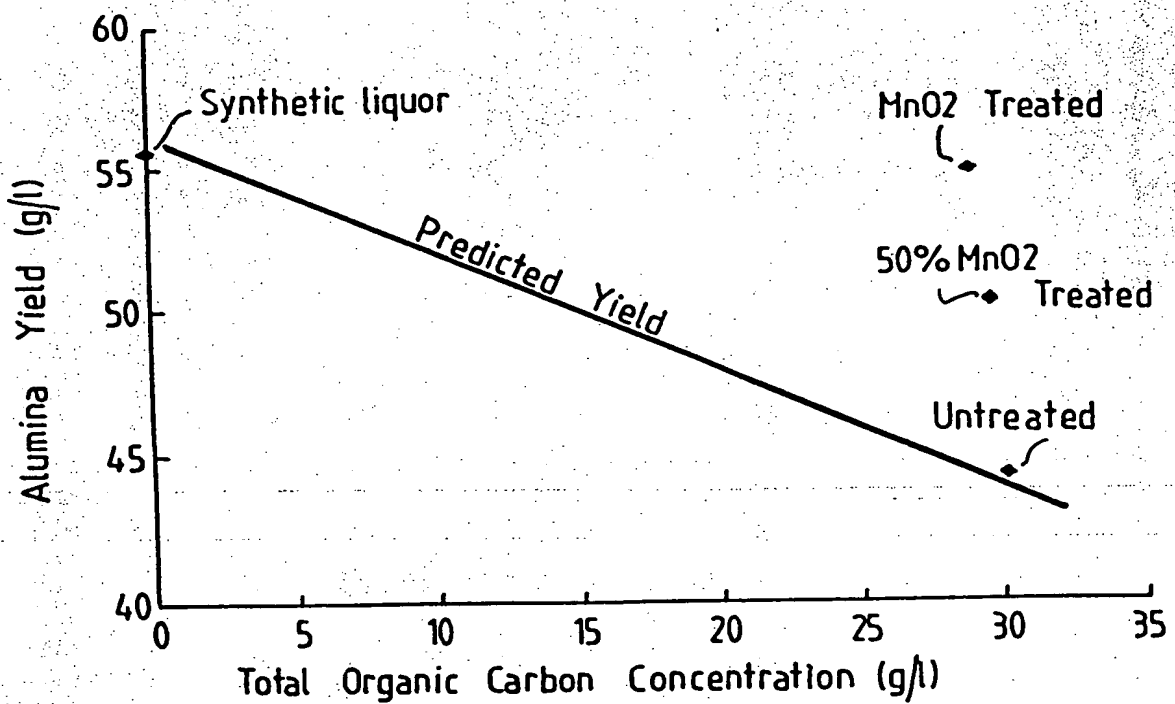
III. 5 . Precipitation rate curves for treatment during bauxite digestion



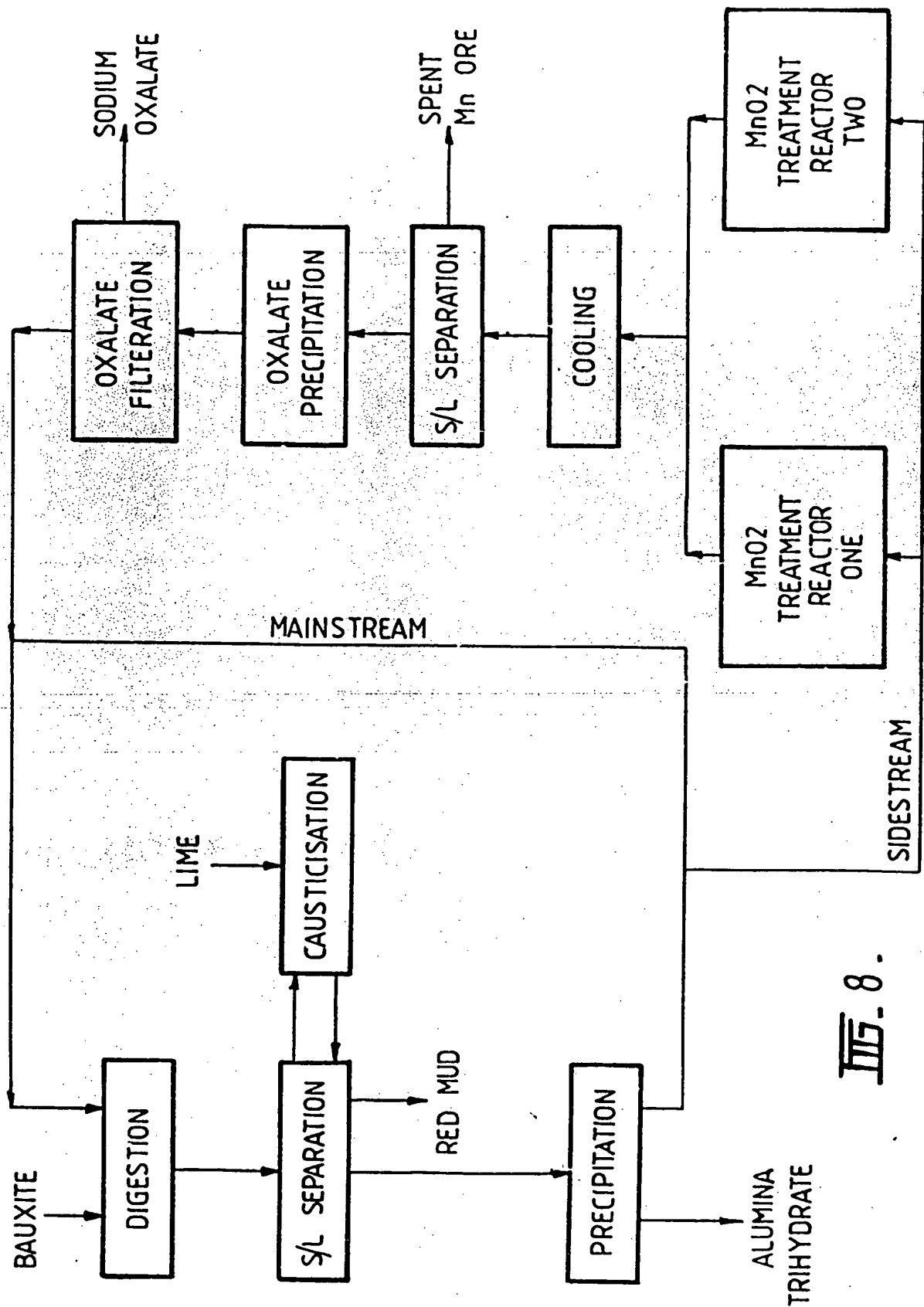
III. 6 . Precipitation rate curves for spent liquors

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III. 7. Comparison of predicted and actual alumina yields

III-8.



AUSTRALIA  
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**PATENT REQUEST : STANDARD PATENT**

We, being the person(s) identified below as the Applicant(s), request the grant of a Standard Patent to the person(s) identified below as the Nominated Person(s), for an invention described in the accompanying complete specification.

**Applicant and  
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**ASSOCIATED PROVISIONAL APPLICATION DETAILS**

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